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International
Journal
Of Modern Engineering Research (IJMER)

Effect of Co doping on the structural and physical properties of $SrC_4H_4O_6.3H_2O$ and $SrC_4H_4O_6.4H_2O$ crystals

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ABSTRACT: *Single crystals of strontium tartrate and cobalt doped strontium tartrate crystals were grown by the single diffusion gel growth technique. The growth conditions were optimized by varying the parameters such as pH, concentration of the gel, gel setting time and concentration of the reactants. Silica gel was used as the growth medium with test tubes as crystallization vessels. Crystals having different morphologies were obtained (transparent and few opaque). The grown crystals were characterized by carrying out PXRD, SXRD, FTIR spectral, UV-Vis-NIR spectral, SHG, PL spectral, AAS, microhardness and TG/DTA measurements. The tri hydrate crystals belong to the monoclinic crystal system and the tetra hydrate crystals belong to orthorhombic crystal system and are optically transparent, NLO active, mechanically soft and thermally stable up to 100 °C. AAS measurement revealed the presence of Co atoms in the doped crystals. Results indicate that Co-doping significantly increases SHG efficiency. Details are presented.*

Keywords: *Gel technique, mechanical properties, optical properties, PXRD, SXRD.*

I. Introduction

Single crystals and polycrystalline form of materials are of great interest, from both solid state sciences aswell as technological point of view.A series of pure and mixed crystals have been grown by several researchers with the aim of identifying new materials for practical and industrial purposes[1]. A systematic study of crystallization in gels began with Liesegang's famous discovery of periodic crystallization in gels [2,3]. The gel technique is an alternative technique to solution growth with controlled diffusion and is free from convection. Gel media prevent turbulence and help in the formation of crystals by providing a framework of nucleation sites[1].

Tartaric acid may serve as a base for the development of new class of materials. Mainly tartrate crystals possess application as dielectric, ferroelectric and piezoelectric materials along with non-linear optical properties [4]. Because of these characteristics, the tartrate crystals are utilised in transducers, linear and non-linear mechanical devices, crystal oscillators and resonators and controlled laser emission [5,6]. Strontium tartrate is used in ammunition units.Some tartrate compounds are used in military applications. The non-linear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Nowadays great attention has been devoted to the growth and characterization of pure and doped tartrate crystals with the aim of identifying new materials for application purposes [7]. Strontium tartrate tetrahydrate crystal is reported to be orthorhombic[8]. Strontium tartrate trihydrate is reported to be monoclinic[9]. The effects of dopants on various properties of single crystals are of great interest for both solid state science as well as technological point of view [7]. Cobalt tartrate crystals have several applications in semiconductors, medicine, optics, gold industries, veterinary drugs, etc[1].

In the present study, single crystals of pure and cobalt doped strontium tartrate tri and tetrahydrate crystals were grown by the gel technique. Optimum growth conditions were determined by varying gel concentration, pH, gel setting time and concentration of reactants. The grown crystals were characterized by carrying out powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SXRD), FTIR spectral, UV-Vis-NIR transmittance spectral, photoluminescence (PL) spectral and atomic absorption spectroscopic (AAS), second harmonic generation (SHG), microhardness and thermogravimetric (TG/DTA) measurements. The results obtained are reported and discussed herein.

II. Growth Of Single Crystals

Good quality single crystals can be grown in gels in a variety of ways; the test tube diffusion method was employed to grow pure and cobalt doped strontium tartrate tri and tetrahydrate crystals. The apparatus used for crystallization consists of borosilicate glass tubes. Silica gel was prepared by adding a solution of sodium meta silicate and tartaric acid by stirring slowly [3]. A fixed amount of gel solution with 1.03g/cm^3 specific gravity and pH was set at 4.0 by adding 0.5M tartaric acid and transferred to several test tubes. The test tubes were sealed. The setting of gel is strongly dependent on pH. High pH value gel takes lower time to set than the low pH value[10].After gel setting, the supernatant solution, strontium chloride of 0.5M was poured over the gel slowly. The test tube was kept undisturbed at room temperature. The supernatant solution diffuses in to the gel column and reacts with the inner reactant, giving rise to the formation of strontium tartrate crystals [6]. We obtain pale yellowish crystals at the bottom of tubes along with transparent and faceted crystals near the gel surface [11]. The chemical reaction is [12,13,14]:

$SrCl_2+C_4H_6O_6 \rightarrow SrC_4H_4O_6+2HCl$

The yellowish crystals were strontium tartrate tetrahydrate(ST4) and the transparent well faceted crystals were strontium tartrate trihydrate(ST3) [11]. For the growth of cobalt doped strontium tartrate crystals, the supernatant solution was a mixture of 0.5M strontium chloride and 0.0025/0.005M cobalt chloride. Slow diffusion of the upper reactant ions through the narrow pores of the silica gel leads to the formation of crystals[14].

Two types of crystals were got in a same test tube due to the change in pH. After the supernatant solution was added, it diffuses in to the gel media and the pH value in the gel surface decreases to 2.6. The bottom layer of the gel remains in the pH value 3.8. It was found that when the pH value is raised from 4.5 to 5, more number of tetrahydrate crystals were obtained. If the pH is lowered to 3, more number of trihydrate crystals can be obtained. The growth of these crystals depends strongly on pH and the specific gravity of the gel. In the discussion hereafter the doped crystals are named as CST31, CST41, CST32 and CST42 (3 for tri and 4 for tetra).

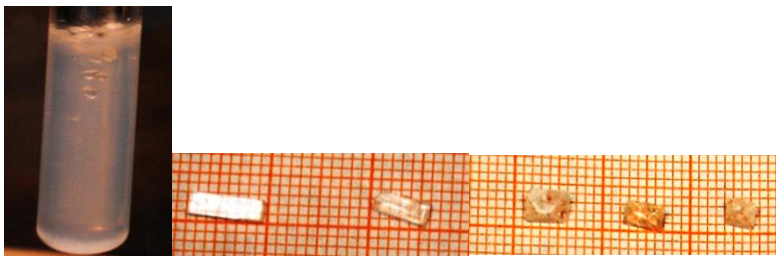
The optimum conditions obtained for the growth of pure and cobalt doped strontium tartrate tetrahydrate crystals are given in Table 1. The crystallographic parameters obtained are provided in Table 2. Figs. 1-3 show the grown crystals of pure and cobalt doped strontium tartrate crystals (ST3,ST4,CST31,CST41, CST32 and CST42).

Table1: Optimum conditions obtained for the growth of pure and cobalt doped strontium tartrate crystals

Parameters	ST3/ST4	CST31/CST41	CST32/CST42
Density of sodium meta silicate (g/cm^3)	1.03	1.03	1.03
Concentration of tartaric acid (M)	0.5	0.5	0.5
pH	4	4	4
Temperature (^{0}C)	30	30	30
Concentration of strontium chloride (M)	0.5	0.5	0.5
Concentration of cobalt chloride (M)	---	0.0025	0.005
Gel setting time (week)	1	1	1
Crystal growth time (days)	25	25	25

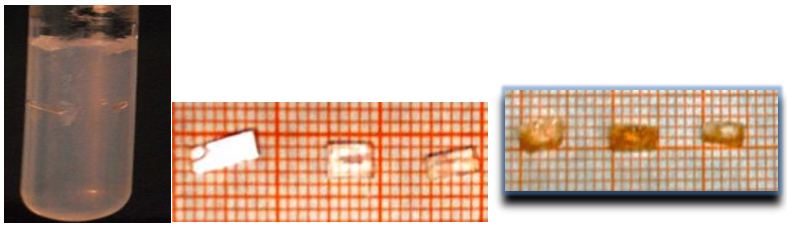
(a) (b) (c)

Fig.1: Photographs showing the (a)growing ST3 and ST4 crystals, (b)grown ST3crystals and (c)grown ST4 crystals



(a) (b) (c)

Fig.2: Photographs showing the (a)growing CST31 and CST41 crystals, (b)grown CST31 crystals and (c)grown CST41 crystals



(a) (b) (c)

Fig.3: Photographs showing the (a)growing CST32 and CST42 crystals, (b)grown CST32 crystals and (c)grown CST42 crystals

III. PXRD and SXRD Analysis

The PXRD patterns were recorded using an automated X-ray powder diffractometer with Cu Kα (λ=1.54056 Å) radiation. The indexed (using a software) PXRD patterns are shown in Fig.4.The crystallinity of the crystals are quite clear from the occurance of sharp peaks at specific Bragg angles. SXRD data were collected using an EnrafNonius CAD4-F diffractometer. Lattice parameters were determined and the crystal system was identified. The SXRD analysis indicates that the cell parameters obtained for the pure crystals are closely matching with the values already reported [8,9]. No significant variation of lattice parameters due to doping is observed which indicates that cobalt doping does not lead to any serious lattice distortion. However, the small increase in lattice volume observed due to doping indicates that the cobalt atoms have entered into the strontium tartrate crystal matrix.

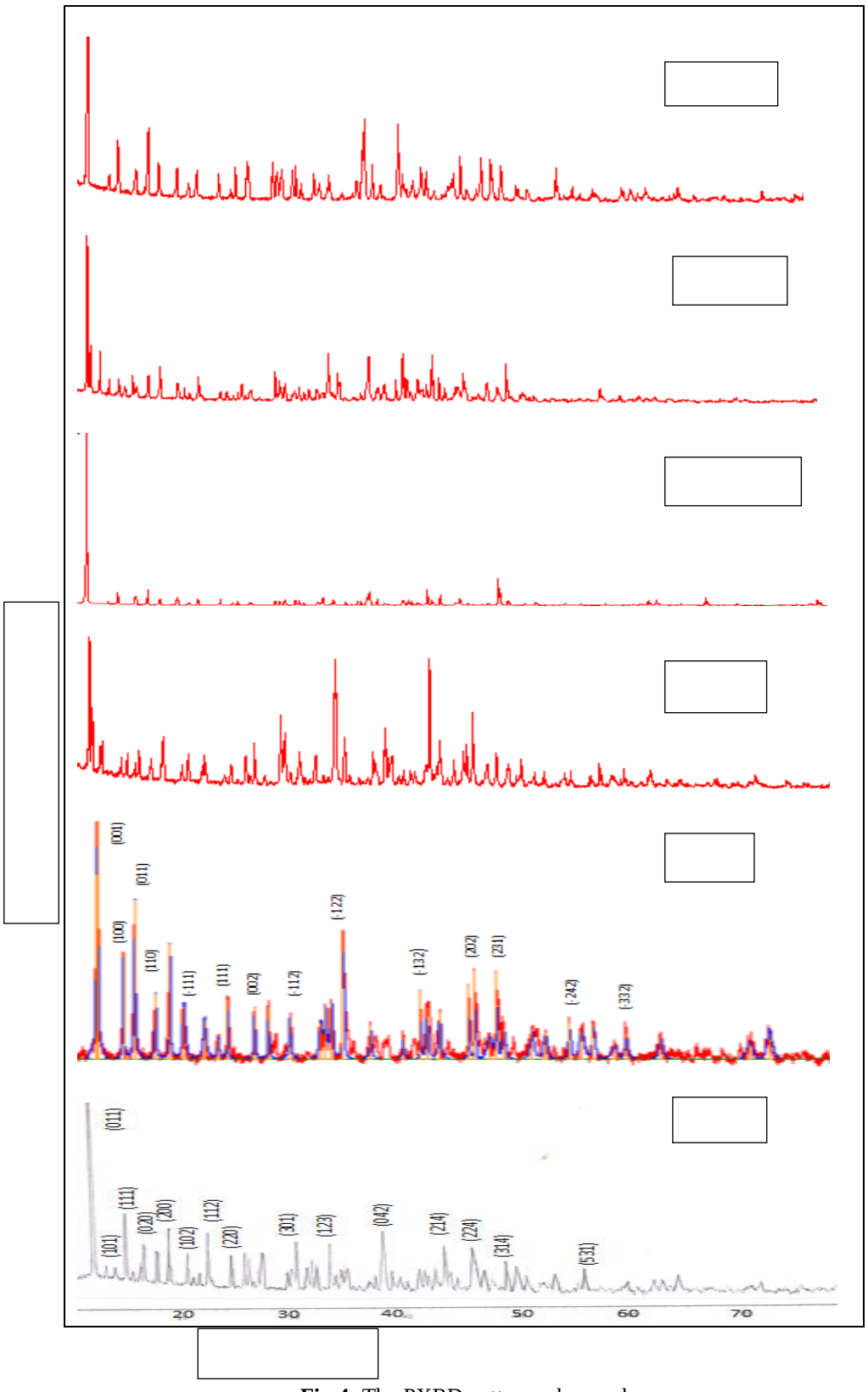


Fig.4: The PXRD patterns observed

Table2: Crystallographic parameters for pure and cobalt doped strontium tartrate crystals

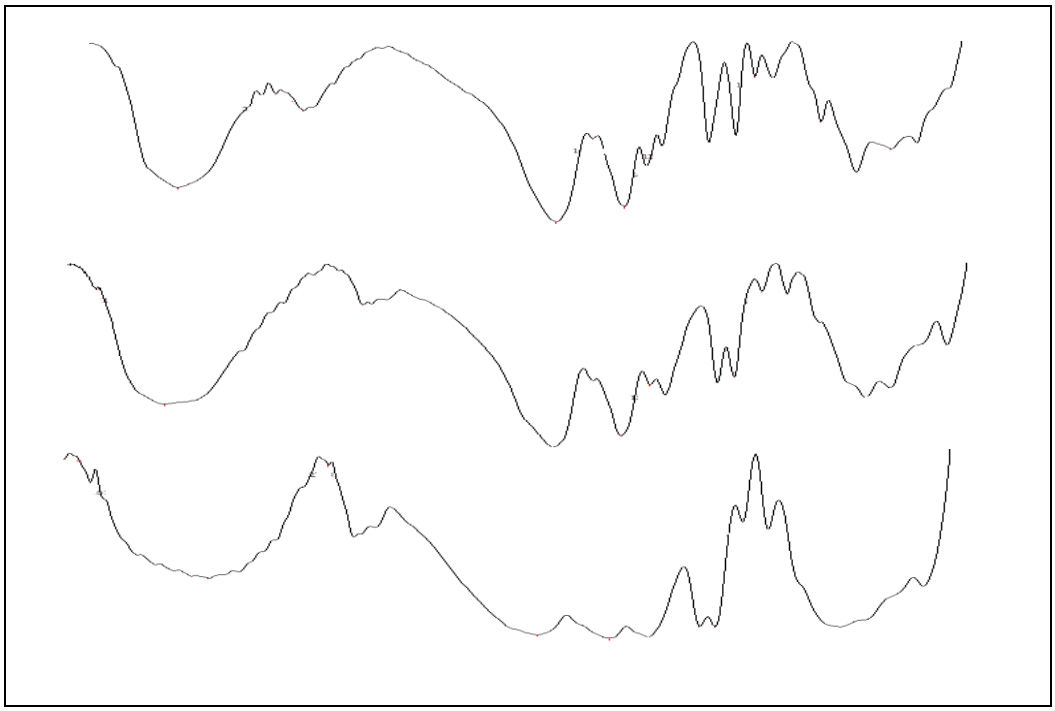
Parameters	Pure(ST3)		Pure(ST4)		CST31	CST41	CST32	CST42
	Reported [9,11]	Present work	Reported[8]	Present Work				
a(Å)	7.55	7.47	9.48	9.47	7.48	9.44	7.48	9.47
b(Å)	10.06	10.03	10.96	10.92	10.03	10.91	10.04	10.92
c(Å)	6.47	6.44	9.46	9.39	6.47	9.49	6.50	9.50
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	Orthorhombic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
Volume(Å^3)	491.42	482.51	984.98	971.04	485.41	977.38	488.14	982.42

IV. FTIR Spectral and AAS Analysis

The FTIR spectra were recorded by employing a SHIMADZU spectrometer in the wave number range 400-4000cm^{-1}for the grown crystals are shown in Fig. 5. Due to the small dopant concentration, there is no significant difference observed for the doped crystals.

The O-H stretching frequency of the sample appears at 3400 cm^{-1}[1]. The bands at 3200 cm^{-1} are assigned to C-H stretching vibrations [10,14,15]. This indicates the presence of water and it belongs to free water symmetry stretch. The strong C-O stretch has been found around 1399cm^{-1} [6]. C-O-C asymmetric strong stretching has been observed in the range 1300-1270cm^{-1}[6]. The band at 1591cm^{-1}is attributed to the C-O stretch of carbonyl group [6,16].

The AAS analysis carried out by using a Perkin Elmer spectrophotometer indicates the presence of cobalt in the doped crystals. The Co content present in the crystal is nearly proportional to the concentration considered in the solution used for the growth of single crystals. It is found that the tetrahydrate crystals are having high cobalt content than the trihydrate crystals (see Table 3).



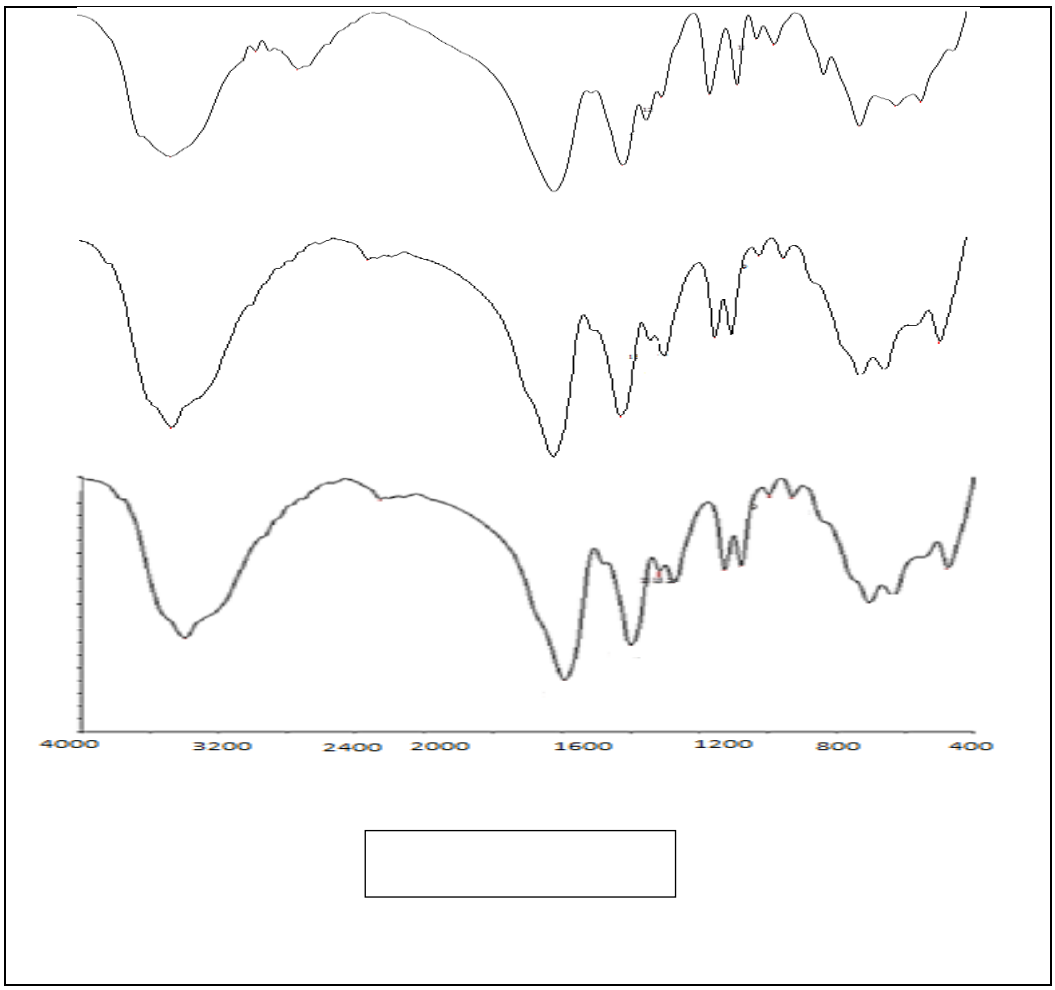


Fig.5 : The FTIR spectra(From top CST31, CST41, CST32, CST42, ST3 and ST4)

V. Optical Properties

Single crystal is mainly used in opto-electronic applications. So, the optical transmission range and transparency cut-off wavelength are essential [17]. UV-Vis-NIR transmittance spectra (shown in Fig. 6) of pure and cobalt doped strontium tartrate crystals dissolved in water were recorded using a SHIMADZU UV-2450 UV-Visible Spectrophotometer in the wavelength range 200-1100nm. From the spectra it can be seen that these crystals have sufficient transmission in the entire visible and most of the UV regions. There is a transparency around 250nm which shows that thesecrystals are suitable for second harmonic generations[18].Efficient nonlinear optical crystals have an optical transparency lower cut off wavelengths between 200 and 400nm. From this, it can be understood that these crystals can be considered as promising nonlinear optical (NLO) crystals.

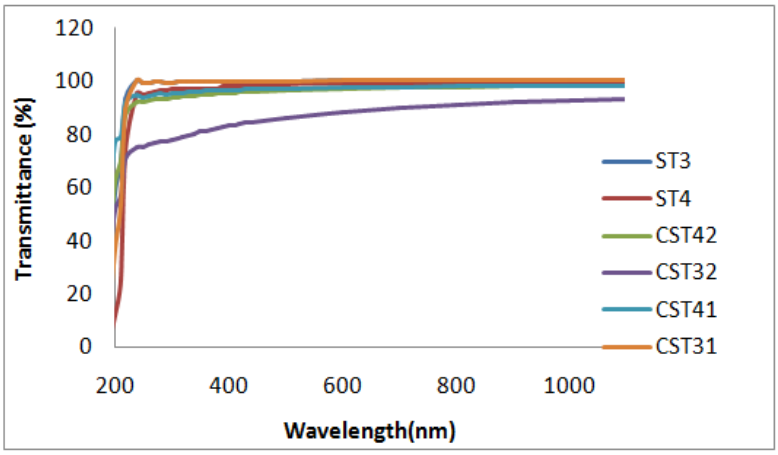


Fig.6: The observed UV-Vis-NIR spectra

The second harmonic generation property was tested for the grown crystals by passing the output of Nd-YAG Quanta ray laser through the crystalline powder sample. The SHG efficiencies observed for the grown crystals are given in Table 3. All the grown crystals are observed to be NLO active.The SHG efficiency increases very significantly due to doping.

Photoluminescence spectra (shown in Fig. 7) were recorded using a Perkin Elmer LS55 fluorescent spectrophotometer at room temperature. The spectra show three peaks at 390, 520 and 770nm. Most intense peak is at 390nm which is the violet emission. Peak at 520 nm, the green emission is less intense and there is red emission at 780nm having sharp peak [4]. It can be seen that the grown crystals are having the fluorescent property. The maximum PL yield is observed for the ST4 crystal.

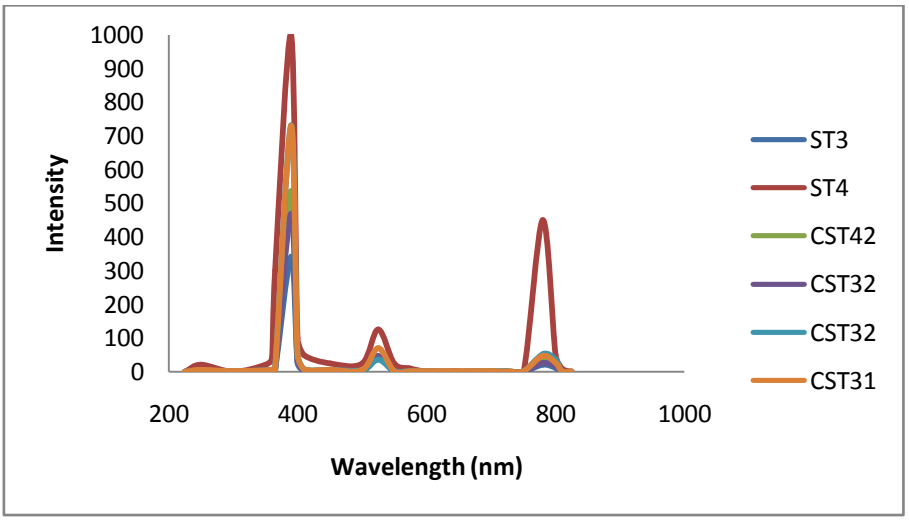


Fig.7: The observed emission (PL) spectra

VI. Mechanical Properties

The Vicker's hardness number (H_v) is defined as

$H_v=1.8544\ P/d^2$ kg/mm^2 [19,20]

Here P is the load applied and d is the diagonal length of the indentation made on the crystal surface.

The Vicker's hardness numbers(H_v) observed (by carrying out the microhardness measurements using a Shimadzu HMV-2 microhardness tester) for various loads(P) in the present study for all the 6 crystals grown are shown in Fig. 8. It is found that the hardness number increases with the increasing load. Also, the hardness numberis found to be more for the trihydrate crystals than for the tetrahydrate crystals.

The work hardening coefficients(n), were determined from the slopes of log P vs log d Plots(not shown here) .The values of n are found to be >2 (see Table 3). According to Onitsch and Hanneman 'n' should lie between 1.0 and 1.6 for hard materials and above 1.6 for soft ones [19].The 'n' values observed in the present study indicate that all the crystals grown belong to soft materials category.

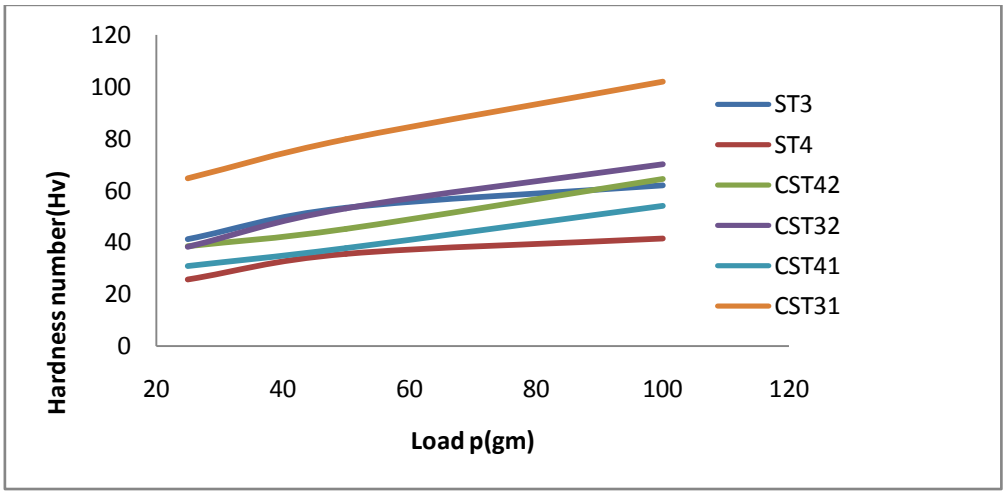


Fig.8: The hardness behaviour

Table 3: The observed SHG efficiencies, work hardening coefficients (n) and Co atom contents (from AAS analysis)

Name of the crystal	SHG efficiency (KDP unit)	n	Co atom content (ppm)
ST3	0.58	2.7	-----
ST4	0.55	3.1	-----
CST31	0.98	3.1	7.98
CST41	1.23	3.2	73.58
CST32	0.93	3.5	10.36
CST42	1.18	3.1	190.13

VII. Thermal (TG/DTA) Analysis

The TGA and DTA patterns recordedby using a thermal analyser (model SDT-Q600)for the pure and doped crystals in the temperature range 50 to 800°C are shown in Fig. 9. It is found that the material is stable up to 100°C. The decomposition process starts at 100°C and this continues up to 220°C. This is due to the removal of entrapped lattice water[5]. Then it remains stable up to 250°C. After that the second decomposition starts and extends up to 340° C resulting in the formation of strontium oxalate (SrC_2O_4). The third decomposition starts at 380° C and ends at 450°C resulting in the formation of strontium carbonate($SrCO_3$)[8]. The water molecules ejected during the first decomposition stage and are in confirmity with the IR spectral studies.

DTA curve shows an endothermic peak (around 170°C for ST4 and ST3 crystals and 140°C for CST42 and CST32 crystals) corresponding to the elimination of the water molecules. Thermal decomposition reactions are usually endothermic. Exothermic peak (around 440°C for ST4 and ST3 crystals and 410°C for CST42 and CST32 crystals) is due to the oxidation reaction taking place along with decomposition.

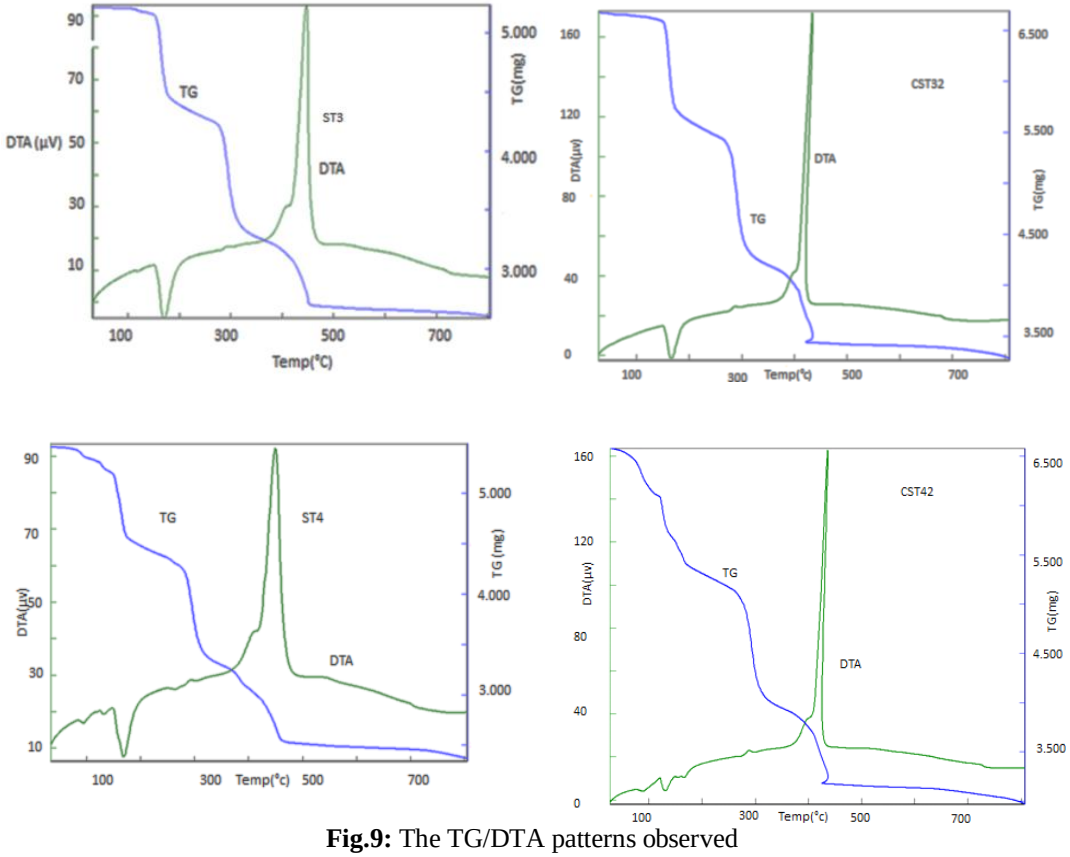


Fig.9: The TG/DTA patterns observed

VIII. Conclusions

Pure and cobalt doped strontium tartrate crystals have been grown successfully by the single diffusion gel growth technique. It was found that the number of tetrahydrate crystals decreases during doping process.Tri and tetrahydrate crystals were obtained due to the change in pH in the test tube during the diffusion of the supernatant solution. The pure and cobalt doped strontium tartrate tetrahydrate crystals are found to be pale

yellow and the trihydrate crystals are transparent in nature and are of good quality crystals. PXRD confirms the crystallinity of the grown crystals. SXRD confirms the orthorhombic crystal system for the growntetrahydrate and monoclinic for the trihydrate crystals. Unit cell parameters of the undoped (pure) crystals match well with the reported SXRD standard values. AAS confirms the presence of cobalt in the doped crystals. It is found that the doped tetrahydrate crystals are having high cobalt concentration. The grown crystals show a wide optical transparency above 250 nm and are found to be useful for the second harmonic generation. Cobalt doping is found to increase the SHG efficiency very significantly. Photoluminescence spectra show that the grown crystals are having the luminescent nature. Microhardness test reveals that the grown crystals belong to soft materials category. The grown crystals are found to be thermally stable at least up to 100 °C. The present study indicates that the optical and mechanical properties of strontium tartrate (both trihydrate and tetrahydrate) single crystals can be tuned significantly by cobalt doping.

REFERENCES

[1] Mathivanan.V, Haris.M, Prasanyaa.T and Amgalan.M (2014) Synthesis and characterization of gel-grown cobalt tartrate crystals. *Pramana- journal of physics, V-82, No.3*,pp(537-548).

[2] Heinz K Henisch (1988) *Crystals in Gels and Liesegang Rings* (Cambridge University Press, Cambridge).pp(2).

[3] Suresh KedaBachhav, PadmakarArjunDavale and Suresh TrimbakPawar (2010) Growth and study of BaTr single crystals by gel technique. *Advances in Applied Science Research*, 1(1), pp(26-33).

[4] Sawant.D.K, Patil.H.M, Bhavsar.DD, Patil.J.H and Girase.K.D (2011). SEM, PL and UV properties of mixed crystals of Ca-Ba tartrate in Silica gel. *Der ChemicaSinica2(3):63-69*

[5] Firdous A, Quasim I, Ahmad M M and Kotru P N (2010) Dielectric and thermal studies on gel grown strontium tartrate pentahydrate crystals. *Bull.Mater.Sci*, 33(4), pp(377-382).

[6] Mary Freeda M, Krishna Priya R, Freeda T H and Mary Delphine S (2012) Crystallization and characterization of mixed crystals of strontium calcium barium tartrate. *Archives of Applied Science Research*, 4(1), pp(128-136).

[7] Suresh Kumar B, Rahim Kutty M H, Sudarsana Kumar M R and RajendraBabuK (2007) Growth and characterization of pure and lithium doped strontium tartrate tetrahydrate crystals by solution-gel technique. *Bull. Mater. Sci*., 30(4), pp(349-355).

[8] Rahim Kutty M H, RajendraBabu K, SreedharanPillai K, Sudarsana Kumar M R, and Nair C M K (2001) Thermal behaviour of strontium tartrate single crystals grown in gel. *Bull. Mater. Sci.*, 24(2), pp (249-252).

[9] Ambady G K (1968) The crystal and molecular structures of strontium tartrate trihydrate and calcium tartrate tetrahydrate.*ActaCryst.*,B24, pp(1548).

[10] Mathivanan V, HarisM(2013) Investigation of sodium potassium bitartrate crystals grown in silica gel and its characterization. Optic-*Int. J. Light Electron Opt.(2013)*

[11] Arora S K, Vipul Patel, Brijesh Amin and Anjana Kothari (2004) Dielectric behaviour of strontium tartrate single crystals. *Bull. Mater. Sci.*, 27(2), pp(141-147).

[12] Angel Mary Greena J, SahayaShajan X and Alex Devadoss H (2010) Electrical conductivity studies on pure and barium added strontium tartrate trihydrate crystals. *Indian Journal of Science and Technology*, 3(3), pp(250-252).

[13] VijayaKumari.T, Padma.C.M and Mahadevan.C.K (2014) Optical and mechanical properties of pure and manganese doped strontium tartrate tetrahydrate single crystals. *Int. Journal of Engineering Research and Applications, V-4, Issue-2(Version 4), pp(47-52).*

[14] Sachin J.Nandre, ShardaJ.Shitole and RajendraR.Ahire(2013) Structure, surface morphology and thermal study of strontium tartrate crystals grown in silica gel by single diffusion method. *Adv. In Applied Science Research, 4(5) 00(223-231).*

[15] Joshi S J, Parekh B B, Vohra K D and Joshi M J(2006), Growth and characterization of gel grown pure and mixed iron-manganese levo-tartrate crystals. *Bull. Mater. Sci.* V-29, N0-3, pp(307-312).

[16] SahayaShajan X and Mahadevan C (2004) On the growth of calcium tartrate tetrahydrate single crystals. *Bull. Mater.Sci.*,27(4), pp(327-331).

[17] Cynthia. S and Milton Boaz. B(2013) Synthesis growth and Characterization of a Novel Non-Linear Optical Crystal: Cadmium Mercury ThiocyanateDimethylsulphoxide. *Journal of Applied Physics V-3, Issue 6, pp(06-11).*

[18] Sawant D K and Bhavsar K S (2012) Photo-luminescence and band gap energy of Ca-Sr tartrate. *Archives of Physics Research*, 3(1), pp(29-35).

[19] Kavitha J M and Mahadevan C K (2013) Growth and characterization of pure and glycine added morenosite single crystals. *Int. J. Eng. Res. Appl.(IJERA)*, 3(5), pp(1931-1940).

[20] Anitha Hudson J, Mahadevan C K and Padma C M (2013) Effect of ZnS as an impurity on the physical properties of $(NH_4)H_2PO_4$ single crystals.*Int. Journal of Research in Engineering and Technology V-02, Issue-12, pp(674-683).*